The Influence of Solvents on the Stability Constants of Some Divalent Cation Compounds. Zinc Chlorides in Methanol-Nitromethane, Methanol-Water and Ethylene Glycol (Commemoration Issue Dedicated to Professor Tsunenobu Shigematsu on the Occasion of his Retirement)

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The Influence of Solvents on the Stability Constants of Some Divalent Cation Compounds. Zinc Chlorides in Methanol-Nitromethane, Methanol-Water and Ethylene Glycol

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The stability constants of the monochloro-complex and dichloro-complex of zinc ion in methanol-nitromethane, methanol-water and ethylene glycol, K_1 and K_2, have been determined with the potentiometric method. The result was that K_2 was larger than K_1 in the solvents except ethylene glycol. This may be caused by the transformation from the octahedral to tetrahedral structure. The association constant between zinc and perchlorate ions, K_1^A, was also determined.

KEY WORDS: Stability constants / Zinc chlorides /

INTRODUCTION

Regardnig the chemical association between a divalent metal and a monovalent anion, the stability constant of the mono-complex, K_1, is normally larger than the con stant of the bis-complex, K_2, when the association is ionic. And even if the association is covalent, it is considered that K_1 is larger than K_2 under the similar circumstances of the complexes like configuration and solvation strength.

In the aqueous solution, the hexaaquo- and monochloro-complexes of divalent zinc have the octahedral structure, while in the dichloro- and trichloro-complexes, their structure changes to the tetrahedron.[1] It is interesting to investigate the effect of such structural change on the K_1 and K_2 values in the nonaqueous solvent. In the present study the first and second formation constants of zinc chloride were determined in nonaqueous soivents such as methanol-nitromethane, methanol-water and pure ethylene glycol (E.G.). Methanol as well as water has the structure of polymerization by the hydrogen bond and a considerably larger donner number (DN), but it has a considerably low dielectric constant compared with water. Nitromethane was chosen as a typical aprotic solvent since it has a fairly small DN and a similar dielectric constant to methanol. Furthermore, nitromethane may lack ability to solvate.[2] The dielectric constant of the diol solvent, E. G., is close to that of nitromethane. In pure methanol solvent Hoffmann *et al.* determined K_1 and K_2 values of zinc chloride by a kinetic technique.[3] In their report it was described that the inversion of K_1 and K_2 values ($K_1 < K_2$) may be due

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to the structural change of zinc chloride.

The potentiometric technique is effective when the stability constant has a comparatively large value. But as K_1 and K_2 values of zinc chloride in aqueous solution are fairly low, their reliable value have not yet been got by the potentiometric method. In the present work, the values determined by the solvent extraction method[4] were used for the K_1 and K_2 values in aqueous solution.

DATA TREATMENT AND EXPERIMENTAL SECTION

Zinc perchlorate was prepared by neutralizing the zinc carbonate with perchloric acid and recrystallizing twice from redistilled water. Chloride concentration was controlled by adding sodium chloride or tetraethylammonium chloride. Sodium and tetraethylammonium perchlorates were used to keep the ionic strength constant. All these salts were also purified by recrystallizing them from the suitable solvent. Methanol was purified by being dried with molecular sieves, 3A, and distilled fractionally. Nitromethane was treated with molecular sieves, 5A, followed by filtering and distilling under the reduced pressure. The specific conductances of the purified solvents were $\sim 2\times10^{-7}$, 6.4×10^{-7} and 1.6×10^{-6} $\Omega^{-1}cm^{-1}$ for methanol, nitromethane and water, respectively. Not more than 0.045 weight per cent of water was gaschromatographically detected in the purified methanol.

Sodium chloride[5] in pure methanol and tetraethylammonium chloride[6] and perchlorate[7] in pure nitromethane dissociate almost perfectly into ions. The association constant of zinc and perchlorate ions was obtained by measuring the electric conductance and by treating the obtained data with Fuoss and Edelson method.[8]

The Ag-AgCl electrode was prepared by electrodepositing silver on a platinum wire and electrolyzing it in the hydrochloric acid. As the reference electrode was used Horiba double junction reference electrode, 2535-05T. The potentiometric measurements were performed with Beckman Research pH meter, model 1019. The chemical cell is written as follows:

Ag|AgCl|0.1 *M* KCl aqueous solution|| 0.1 *M* $NaClO_4$ or Et_4NClO_4 in the sample solvent|| sample solution|AgCl|Ag.

All measurements were performed at 25°C.

A) Electric Conductance Experiment

The association constants of zinc perchlorate, K_1^A and K_2^A, are given by;

$$Zn^{2+}+ClO_4^- \overset{K_1^A}{\rightleftharpoons} ZnClO_4^+$$

$$ZnClO_4^+ + ClO_4^- \overset{K_2^A}{\rightleftharpoons} Zn(ClO_4)_2$$

On the assumption that K_1^A is extremely larger than K_2^A, the Fuoss and Edelson equation[8] is expressed for 2-1 electrolyte, MX_2, as follows:

$$\Lambda F = \Lambda_0 - XK_1^A/\Lambda_0 \qquad (1)$$

$$X = cy_{2+}\Lambda F(\Lambda F - \Lambda_0/2)$$

where

F=the Fuoss and Edelson function

Λ_0=the limiting equivalent conductance
Λ=the equivalent conductance
C=the concentration of the anion, ClO_4^-
y_{2+}=the activity coefficient of the divalent cation, $Zn.^{2+}$

B) Potentiometric Experiment

Keeping the concentration of zinc perchlorate constant, the concentration of sodium or tetraethylammonium chloride was changed within the negligibly low concentration range for zinc perchlorate. Then a proper amount of sodium or tetraethylammonium perchlorate was added to keep the ionic strength constant. The chloride concentration, $[C]^-$, of the sample solution was obtained potentiometrically from the calibration curve which was made from the standard solutions with the same ionic strength as that of the sample solution.

In the sample solution the following equilibrium must be considered:

$$Zn^{2+}+ClO_4^- \overset{K_1^A}{\rightleftharpoons} ZnClO_4^+$$
$$Zn^{2+}+Cl^- \overset{K_1}{\rightleftharpoons} ZnCl^+$$
$$ZnCl^+ + Cl^- \overset{K_2}{\rightleftharpoons} ZnCl_2$$
$$ZnClO_4^+ + Cl^- \overset{K_m}{\rightleftharpoons} ZnCl\cdot ClO_4$$

Then, an association constant, K_1^A, is given by:

$$K_1^A = \frac{y_{ZnClO_4}[ZnClO_4^+]}{y_{2+}y_{ClO_4}[Zn^{2+}][ClO_4^-]}$$

where y denotes the activity coefficient for the molarity. As y_{ClO_4} is almost equal to y_{ZnClO_4}, this equation can be written by:

$$y_{2+}K_1^A = \frac{[ZnClO_4^+]}{[Zn^{2+}][ClO_4^-]} \qquad (2)$$

In a similar manner, the other association constants are expressed as follows:

$$y_{2+}K_1 = \frac{[ZnCl^+]}{[Zn^{2+}][Cl^-]} \qquad (3)$$

$$y_{\pm}^2 K_2 = \frac{[ZnCl_2]}{[ZnCl^+][Cl^-]} \qquad (4)$$

$$y_{\pm}^2 K_m = \frac{[ZnCl\cdot ClO_4]}{[ZnClO_4^+][Cl^-]} \qquad (5)$$

where $y_{\pm}^2$ is $y_{Cl}\cdot y_{ZnCl}$ product and this is almost equal to $y_{Cl}\cdot y_{ZnClO_4}$ product.

When C°_{Zn}, C°_{Na} and C°_{Cl} indicate the initial concentrations of $Zn(ClO_4)_2$, $NaClO_4$ (or $(C_2H_5)_4NClO_4$) and NaCl (or $(C_2H_5)_4NCl$), respectively, and if $C^\circ_{Zn} \gg C^\circ_{Cl}$,

$$C^\circ_{Zn} = [Zn^{2+}]+[ZnClO_4^+]$$
$$= [Zn^{2+}] + y_{2+}K_1^A[Zn^{2+}]\{[Zn^{2+}]+C^\circ_{Zn}+C^\circ_{Na}\}$$

This equation is rearranged to

$$[Zn^{2+}] = \frac{-\{1+y_{2+}K_1^A(C^\circ_{Zn}+C^\circ_{Na})\}+[\{1+y_{2+}K_1^A(C^\circ_{Zn}+C^\circ_{Na})\}^2+4y_{2+}K_1^AC^\circ_{Zn}]^{1/2}}{2y_{2+}K_1^A} \qquad (6)$$

Then C°_{Cl} is represented by the following equation,

$$C^{\circ}_{Cl}=[ZnCl^{+}]+[ZnCl\cdot ClO_4]+2[ZnCl_2]+[Cl^{-}]$$
$$=y_{2+}K_1[Zn^{2+}][Cl^{-}]+y^2_{\pm}K_m[ZnClO^{+}_4][Cl^{-}]+2y_{2+}y^2_{\pm}K_1K_2[Zn^{2+}][Cl^{-}]^2+[Cl^{-}]$$

Hence, this equation can be expressed as:

$$C^{\circ}_{Cl}/[Cl^{-}]=n+m[Cl^{-}] \tag{7}$$

Where m and n are given by:

$$m=2y_{2+}y^2_{\pm}K_1K_2[Zn^{2+}] \tag{8}$$

$$n=y_{2+}K_1[Zn^{2+}]+y^2_{\pm}K_m[ZnClO^{+}_4]+1 \tag{9a}$$

or

$$(n-1)/[Zn^{2+}]=y_{2+}K_1+y^2_{\pm}K_m[ZnClO^{+}_4]/[Zn^{2+}] \tag{9b}$$

When $C^{\circ}_{Zn}\gg C^{\circ}_{Cl}$ and when C°_{Zn} and the ionic strength are constant, m and n become constant. Therefore $C^{\circ}_{Cl}/[Cl^{-}]$ *vs.* $[Cl^{-}]$ plots of Eq. (7) should become the linear curves whose slopes and intercepts are m and n, respectively. The m and n values are obtained at a different C°_{Zn}. Then the stability constants, $y_{2+}K_1$, $y^2_{\pm}K_2$ and $y^2_{\pm}K_m$, can be calculated from the plots of m *vs.* $[Zn^{2+}]$ and those of $(n-1)/[Zn^{2+}]$ *vs.* $[ZnClO^{+}_4]/[Zn^{2+}]$. The plot of $(n-1)/[Zn^{2+}]$ *vs.* $[ZnClO^{+}_4]/[Zn^{2+}]$ in pure methanol is shown in Fig. 1.

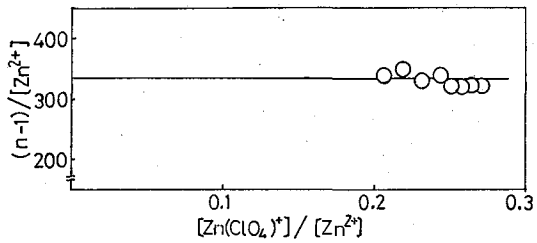

Fig. 1. $(n-1)/[Zn^{2+}]$ *vs.* $[ZnClO^{+}_4]/[Zn^{2+}]$ plot.

As shown in the figure the exact value of $y^2_{\pm}K_m$ was not obtained because of the limited range of $[Zn^{2+}]$, but the slope, $y^2_{\pm}K_m$, was nearly equal to zero. Therefore the assumption that $y_{2+}K_1[Zn^{2+}]\gg y^2_{\pm}K_m[ZnClO^{+}_4]$ is right in the methanol system, and this assumption shall also be reasonable in the present research. Therefore Eq. (9a) can be rewritten as follows:

$$n=y_{2+}K_1[Zn^{2+}]+1 \tag{10}$$

where $[Zn^{2+}]$ can be calculated from Eq. (6). Using Eqs. (8) and (10), $y_{2+}K_1$ and $y^2_{\pm}K_2$ can be easily obtained by the measurements from the sole sample solution having a known C°_{Zn}.

The activity coefficient, y, has been calculated by Debye-Hückel equation:

$$\log y=\frac{-A|Z_+|^2(I)^{1/2}}{1+B\mathring{a}(I)^{1/2}} \tag{11}$$

$$A=1.8246\times10^6/(\varepsilon T/)^{3/2}$$
$$B=5.029\times10/(\varepsilon T)^{1/2}$$

where å is the distance of the closest approach (angstrom unit). The adjustment of C°_{Zn}

and C°_{Na} for the constant ionic strength has been made by Eq. (6) and the following equation:

$$I=2[Zn^{2+}]+C^{\circ}_{Zn}+C^{\circ}_{Na} \tag{12}$$

RESULTS AND DISCUSSION

Fuoss and Edelson plots are shown in Fig. 2, and Λ_0 and K^A_1 values which are given

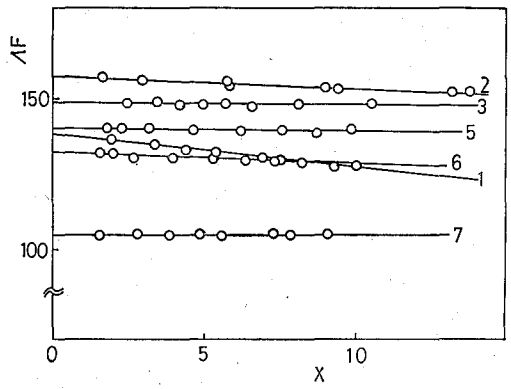

Fig. 2. Fuoss and Edelson plots for zinc perchlorate in each solvent. The numbers in the figure are corresponded to those in Table I.

by the slopes and the intercepts of the linear lines in Fig. 2 are inserted in Table I; W_1 is weight % of the first named member of a pair of solvents. Figure 3 indicates the plots of Λ_0 and K^A_1 *vs.* W_1 in the methanol-nitromethane system. As shown in the figure the Λ_0 value has a maximum at about 20% of methanol. This phenomenon can be explained by the change of the viscosity and that of Stokes radius pointed by Fuoss *et al.*[2] As nitromethane is added to methanol, the value of K^A_1 decreases gradually at first. This is perhaps due to the increase of the solvative monomeric methanol as the progress of the depolymerization of methanol. A similar phenomenon is also observed

Table I. Dielectric Constants, ε, Viscosities, η, Λ_0 and K^A_1 for Each Solvent at 25°C

No.	solvent(W_1)	ε^a	η^b(cp)	Λ_0($cm^2\Omega^{-1}M^{-1}$)	K^A_1(M^{-1})
	CH_3OH-CH_3NO_2				
1	0	36.0	0.622	138	148
2	15	34.05	0.520	157	56
3	40	32.64	0.493	149	10
4	60	32.22	0.499	148	*
5	80	32.31	0.518	141	9
6	100	32.63	0.545	133	53
	CH_3OH-H_2O				
7	90	37.88	0.767	105	*
8	80	42.60	1.006	—	*
9	pure E. G.	37.7	17.33	6.9	*

[a,b] no. 1~6, from ref. 2. no. 7, 8, from ref. 9. [a]no. 9, from ref. 10. [b]no. 9, from Landolt-Börnstein Tabellen (1923) *Completely dissociated.

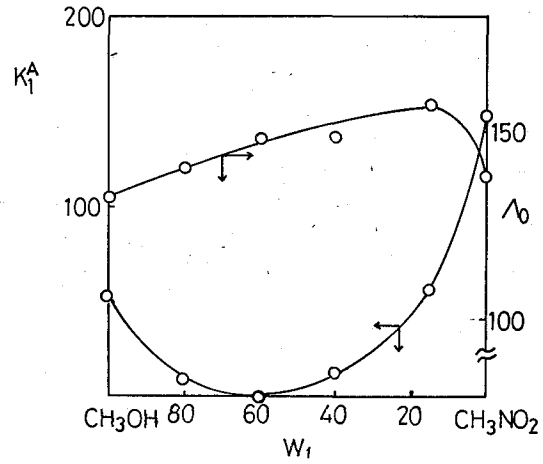

Fig. 3. K_1^A and Λ_0 *vs.* W_1 plots in the methanol-nitromethane system.

in the drop of viscosity. The minimum value of K_1^A occurs when W_1 value of methanol is about 60%. When nitromethane is more added to methanol there appears a sharp increase in K_1^A, and this may be due to lack in the solvative ability of nitromethane.

Some examples of the calibration curves of chloride concentration, $[Cl^-]$, are shown in Fig. 4. The slopes of the curves are in the range of 54.0 to 58.4 in each solvent, and these values are a little lower than the nernstian slope, 59.1. The data for the plots of Eq. (7) are indicated in Table II. The concentration of chlordie, $[Cl^-]$, in the sample solution is calculated from the slope of the calibration curve and the electrode potential of the standard solution with the same ionic strength as that of the sample solution. A typical example of the plots for Eq. (7) is shown in Fig. 5. The lack of the datum in pure nitromethane is due to the low solubility of zinc perchlorate in this solvent.

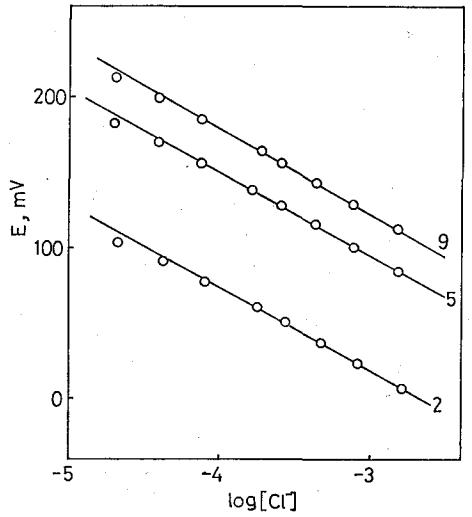

Fig. 4. The calibration curves of chloride concentration, $[Cl^-]$, under the constant ionic strength, (I=0.05).

Table II. Potentiometric Data in Each Solvent at 25°C

No. 2 Solvent (I=0.05)
$C^{\circ}_{Zn}=1.86\times10^{-2}$, $C^{\circ}_{Na}=0$

$C^{\circ}_{Cl}\times10^{4}$	E	$[Cl^-]\times10^{8}$	$C^{\circ}_{Cl}/[Cl^-]$
1.08	258.8	5.36	2010
2.12	248.3	8.20	2590
3.14	241.8	10.7	2930
4.14	237.7	12.6	3290
5.12	234.5	14.2	3580
6.08	232.0	15.8	3850
7.02	229.5	17.5	4010

13.7($[Cl^-]=1.07\times10^{-3}$)[a], S=57.0[b]

No. 3 Solvent (I=0.05)
$C^{\circ}_{Zn}=1.70\times10^{-2}$, $C^{\circ}_{Na}=0$

$C^{\circ}_{Cl}\times10^{4}$	E	$[Cl^-]\times10^{7}$	$C^{\circ}_{Cl}/[Cl^-]$
1.01	239.2	7.54	134
1.98	228.2	12.0	165
2.93	222.1	15.6	188
3.87	217.9	18.7	207
4.78	214.8	21.3	224
5.68	212.1	23.9	238
6.56	210.4	25.7	255

70.1($[Cl^-]=1.02\times10^{-3}$)[a], S=54.0[b]

No. 4 Solvent (I=0.05)
$C^{\circ}_{Zn}=1.67\times10^{-2}$, $C^{\circ}_{Na}=0$

$C^{\circ}_{Cl}\times10^{4}$	E	$[Cl^-]\times10^{6}$	$C^{\circ}_{Cl}/[Cl^-]$
1.01	239.8	4.31	23.4
1.98	227.4	7.19	27.5
2.93	220.4	9.60	30.5
3.87	216.0	11.5	33.7
4.78	212.2	13.5	36.1
5.68	209.5	15.0	37.9
6.56	207.8	16.5	39.8

107.8($[Cl^-]=1.02\times10^{-3}$)[a], S=55.8[b]

No. 5 Solvent (I=0.05)
$C^{\circ}_{Zn}=1.70\times10^{-2}$, $C^{\circ}_{Na}=0$

$C^{\circ}_{Cl}\times10^{4}$	E	$[Cl^-]\times10^{6}$	$C^{\circ}_{Cl}/[Cl^-]$
1.01	217.9	7.99	12.6
1.98	205.5	13.0	15.2
2.93	197.6	17.8	16.5
3.87	192.4	21.8	17.8
4.78	188.8	25.2	19.0
5.68	185.3	28.9	19.7
6.56	182.8	31.9	20.6

95.4($[Cl^-]=1.02\times10^{-3}$)[a], S=58.4[b]

No. 6 Solvent (I=0.135)
$C^{\circ}_{Zn}=4.5\times10^{-2}$, $C^{\circ}_{Na}=0$

$C^{\circ}_{Cl}\times10^{4}$	E	$[Cl^-]\times10^{5}$	$C^{\circ}_{Cl}/[Cl^-]$
2.26	216.2	1.38	16.4
3.55	207.0	2.10	16.9
4.94	200.3	2.85	17.3
6.42	194.8	3.66	17.5
7.95	190.8	4.39	18.1

188.3($[Cl^-]=4.92\times10^{-5}$)[a], S=50.5[c]

No. 7 Solvent (I=0.1)
$C^{\circ}_{Zn}=3.33\times10^{-5}$, $C^{\circ}_{Na}=0$

$C^{\circ}_{Cl}\times10^{4}$	E	$[Cl^-]\times10^{5}$	$C^{\circ}_{Cl}/[Cl^-]$
1.97	178.7	6.13	3.21
3.29	168.2	9.89	3.33
4.81	160.7	13.9	3.46
6.49	154.4	18.6	3.49
8.31	149.6	23.1	3.60

170.4($[Cl^-]=7.59\times10^{-5}$)[a], S=50.5[c]

No. 8 Solvent (I=0.1)
$C^{\circ}_{Zn}=3.33\times10^{-2}$, $C^{\circ}_{Na}=0$

$C^{\circ}_{Cl}\times10^{4}$	E	$[Cl^-]\times10^{4}$	$C^{\circ}_{Cl}/[Cl^-]$
3.27	163.0	1.64	1.99
5.08	154.4	2.42	2.10
7.10	147.7	3.29	2.16
9.29	142.2	4.22	2.20
11.6	137.6	5.21	2.23

176.4($[Cl^-]=8.88\times10^{-5}$)[a], S=50.5[c]

No. 9 Solvent (I 0.05)
C°_{Zn} 1.67×10^{-2}, C°_{Na} 0

$C^{\circ}_{Cl}\times10^{4}$	E	$[Cl^-]\times10^{5}$	$C^{\circ}_{Cl}/[Cl^-]$
1.01	202.8	4.04	2.50
1.98	186.1	7.90	2.51
2.93	176.6	11.6	2.53
3.87	169.9	15.2	2.55
4.78	164.6	18.7	2.56

129.8($[Cl^-]=7.59\times10^{-4}$)[a], S=57.3[b]

[a]E-values and $[Cl^-]$ of the standard solutions. [b]The slopes for the Ag-AgCl electrode. [c]The slopes for the Cl^-electrode of Tôkô Chem. Labo. Co., Ltd.

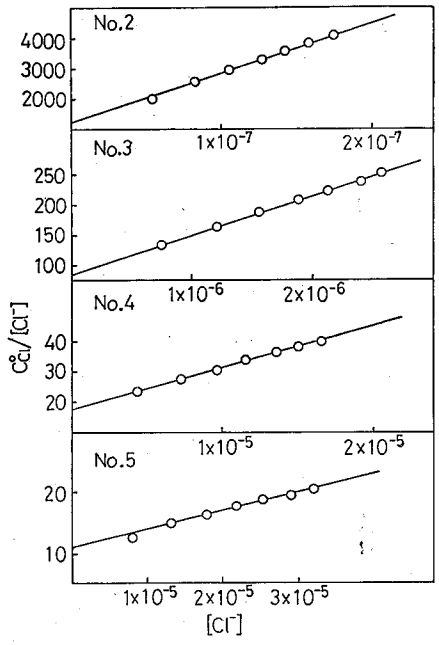

Fig. 5. $C^{\circ}_{c1}/[Cl^-]$ *vs.* $[Cl^-]$ plots.

The comparion of the true stability constants, K_1 and K_2, is more reasonable than that of $y_{2+}K_1$ and $y_{\pm}^2K_2$ under the arbitray ionic strength. Therefore there is necessity to know the activity coefficients, y_{2+} and $y_{\pm}$. However we are in great want of the data on the activity coefficicnts in non-aqueous solvents. Thus the activity coefficients must be calculated using Debye-Hückel equation (Eq. 11). The calculated activity coefficients, y_{2+} and $y_{\pm}$, and stability constants, K_1 and K_2, are listed in Table III.

The plots of log K_1 and log K_2 *vs.* W_1 are given in Fig. 6. The values of K_1 and K_2 in pure water have been got from Ref. 4. The figure indicates that K_2 is larger than K_1 in the whole range of W_1. The K_1 value scarcely changes over 70% of methanol. The K_2/K_1 ratio in the methanol-nitromethane mixtures increases gradually as the amount of nitromethane increases. The plots of log K_1 and K_2 *vs.* $100/\varepsilon$ in the

Table III. Activity Coefficients and Stability Constants at 25°C

No.	I	y_{2+}(Å)[a]	$y_{\pm}$(Å)[a]	$y_{2+}K_1$	$y_{\pm}^2K_2$	K_1	K_2
2	0.05	0.0945(5)	0.516(3.5)	7.25×10^4	7.37×10^6	7.7×10^5	2.8×10^7
3	0.05	0.0900(5.5)	0.510(4)	3.70×10^5	5.30×10^3	5.9×10^4	1.4×10^6
4	0.05	0.0939(6)	0.504(4)	1.00×10^3	4.07×10^4	1.1×10^4	1.6×10^5
5	0.05	0.0947(6)	0.506(4)	6.30×10^2	1.41×10^4	6.7×10^3	5.5×10^4
6	0.135	0.0482(6)	0.398(4)	3.40×10^2	2.17×10^3	7.1×10^3	1.4×10^4
7	0.1	0.0969(6)	0.500(4)	6.4×10	4.8×10^2	6.6×10^2	1.9×10^3
8	0.1	0.134(6)	0.552(4)	3.0×10	2.2×10^2	2.2×10^2	7.2×10^2
9	0.05	0.145(6)	0.575(4)	8.8×10	1.5×10^2	6.1×10^2	4.6×10^2

[a]The distances of the closest approach roughly estimated with reference to the data of the distances in water and other organic solvents.

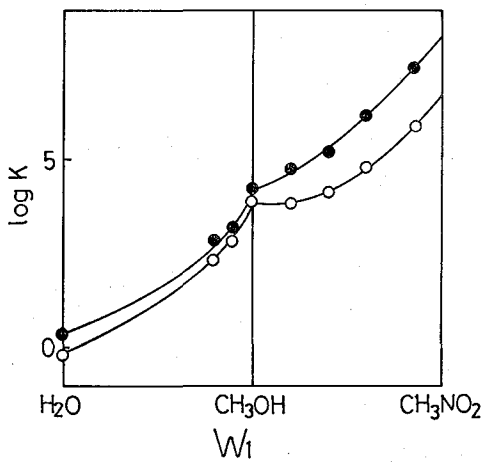

Fig. 6. log K *vs.* W_1 plots in the methanol-nitromethane and methanol-water systems.
○ K_1, ● K_2.

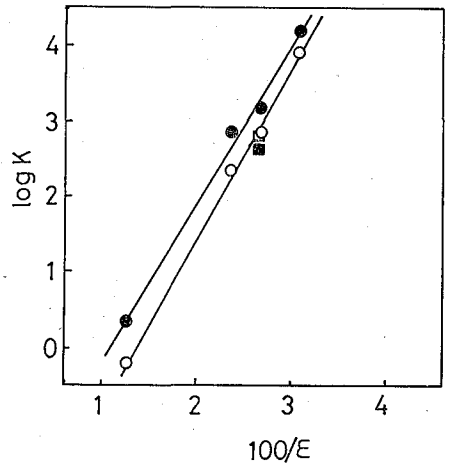

Fig. 7. log K *vs.* 100/ε plots.
○ K_1, ● K_2 in methanol-water. □ K_1, ■ K_2 in ethylene glycol.

methanol-water and pure ethylene glycol systems are given in Fig. 7. The good ilnearity of the plots in Fig. 7 except the deviation of K_2 in pure ethylene glycol indicates that the association between zinc and chloride ions may have fairly ionic character.

Divalent zinc ion with the d^{10} electron configuration does not have the crystal field stabilization energy, and the structure of the zinc complexes is dependent on the mutual interaction between the ligands. When the first chloride ligand coordinates to octahedral hexaaquozinc(II) ion in water, the five solvated water molcules of the formed monochlorozinc(II) ion must become more labile because of the bulk and charge of chloride ion. Therefore the second chloride ligand can coordinate easily, and dichlorozinc compound may change to the tetrahedral structure owing to the large hindrance between the ligands. As indicated in Fig. 6, K_2 is always larger than K_1 in the methanol-nitromethane mixture. This indicates that the structural change will occur in the

methanol-nitromethane mixture as well as in water. This phenomenon will be more notable in nitromethane than in methanol owing to the bulk and weak solvation ability of nitromethane. And as the nitromethane content increases, such tendency will get stronger as understood from the increase of the K_2/K_1 ratio.

The result that the K_1 value is larger than the K_2 value in ethylene glycol may indicate the low hindrance between the ligands of the monochloro-complex, and the configuration in the formation of the dichloro-complex will not change, though the configuration is not evident. Namely zinc ion in ethylene glycol may have enough spaces to substitute the chloride ligands for the solvated ethylene glycol molecules, and mainly the electrostatic force between the cation and the anion may become an important factor to govern the K_1 and K_2 values.

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